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Interfacial enhancement of nano-SiO_2/polypropylene composites

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ABSTRACT

The authors proposed an approach for manufacturing nano-SiO_2/polypropylene (PP) composites by in situ reactive processing. The key issue lies in that the nanoparticles were covalently bonded to the matrix polymer via polyurethane (PU) elastomer and PP-g-NH_2. Unlike the previous techniques based on graft polymerization, the present one did not need to pretreat the nanoparticles. Taking the advantages of rubber-type grafting polymer (i.e. PU) and interfacial reactive compatibilization with PP-g-NH_2, a synergetic toughening effect was observed for the PP nanocomposites. Only very low concentrations of nano-SiO_2 (1.5–2.5 vol.%) and PU (<4 vol.%) were sufficient to greatly increase notched impact strength of PP. Meanwhile, tensile properties of the nanocomposites were also slightly enhanced.

1. Introduction

As a new class of material, polymer-based nanocomposites are able to offer significant improvement in physical and engineering properties at low filler loading [1–9]. Because commercially available nanoparticles are generally agglomerated as a result of their high surface energy, breakdown of nanoparticle agglomerates before or during composites fabrication proves to be a key issue to bring the nanoparticles into full play [10]. In addition, switching the surface feature of nanoparticles from hydrophilic to hydrophobic for increasing the filler/polymer matrix compatibility is also critical.

Our previous works demonstrated that graft polymerization onto nanoparticles is an effective way to fulfill the above requirements [1,10,11]. By changing species of grafting monomer and conditions of grafting, interfacial interaction in nanocomposites can be purposely adjusted. Nanocomposites with desired properties can be acquired accordingly [12]. For further toughening nano-$CaCO_3$/polypropylene (PP) composites, for example, Ma et al. grafted elastomer (i.e. poly(butyl acrylate) (PBA)) onto the nanoparticles and observed a significant enhancement of notched impact strength of the composites [13]. Meanwhile, Zhou et al. developed a reactive compatibilization approach when producing nano-SiO_2/PP composites [14]. The nanosized filler was grafted with poly(glycidyl methacrylate) (PGMA) and then melt-mixed together with PP and functionalized PP (PP-g-NH_2). Because the epoxide (of PGMA) reacted with amine groups (of PP-g-NH_2) during compounding, nano-SiO_2 was linked to the matrix as a result. Similar enhancement of nano-filler/polymer compatibilization can also be achieved by using maleic anhydride grafted PP (PP-g-MA) as compatibilizer [2].

In fact, the above two methods still have defects. When PBA was grafted onto the nanoparticles, physical interaction between the polar grafted polymer chains and the non-polar matrix was not strong enough. As a result, tensile strength of the composites was reduced compared to that of unfilled matrix PP [13]. As for the nanocomposites made via reactive compatibilization, the grafted PGMA lacked flexibility, so that the composites' failure strain was deteriorated [14].

The authors of the present work proposed a new technique that combines the above idea of using elastomer as grafting polymer with reactive compatibilization to manufacture PP based nanocomposites, in hopes of yielding an overall improvement of the mechanical properties. Firstly, polyurethane (PU) elastomer is blended with nano-SiO_2 in the presence of PP at elevated temperature to initiate the reaction between isocyanate (of PU) and hydroxyl (of the nanoparticles) [15,16]. As a result, PU can be in situ grafted onto nano-SiO_2. Then, the PP based masterbatches containing PU grafted nano-SiO_2 are melt compounded with reactive compatibilizer PP-g-NH_2. Owing to the reaction between the amino groups and PU, the nanoparticles are thus covalently connected to the matrix. To provide the interphase with sufficient extensionality, excessive PU (relative to nano-SiO_2) should be employed. Feasibility of the proposed technique is evaluated hereinafter in terms of studying structure and mechanical properties of the resultant nanocomposites.

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2. Experimental

2.1. Materials

Nano-silica (Aerosil 200; average diameter = 12 nm, specific surface area = 200 m^2/g) was supplied by Degussa Co., Germany. The particles were vacuum dried at 120 °C for 24 h to eliminate the adsorbed species. Isotactic PP homopolymer (trade name: HJ400®) with a melt flow index (MI) of 8 g/10 min (ASTM D-1238) provided by Samsung Total Petrochemicals Co. Ltd., Korea, was used as the matrix polymer of the composites. Maleic anhydride grafted PP (PP-g-MA, grafting percentage = 1 wt.%) was supplied by Ketong Plastics Technology Co. Ltd., China.

Hexamethylenediamine (HMDA), toluene diisocyanate (TDI), and methylene-bis-ortho-chloroaniline (MOCA) were acquired from Shanghai Wulian Chemical Co. Ltd., China. Polyoxypropylene glycol (PPG, number average molecular weight = 2000) was supplied by Jinling Petrochemical Company of Nanjing, China.

2.2. Preparation of PP-g-NH_2 and PU prepolymer

PP-g-NH_2 was prepared according to the method proposed by Lu et al. [17]. In brief, rough PP-g-NH_2 was obtained by melt mixing of PP-g-MA and HMDA (1:1.5 by molar ratio of MAH to diamine) via an instrumented batch mixer (Haake Rheocord 300p, mixing temperature = 180 °C, rotor speed = 60 rpm, and mixing time = 10 min). Then, the resultant was dissolved in refluxing toluene at a concentration of 4% (wt./vol.) and precipitated in ethanol at room temperature to remove residual HDMA. The dissolution–precipitation procedure was repeated for three times. Finally, the purified PP-g-NH_2 was vacuum dried at 60 °C. By acid–base titrations, the content of HMDA introduced onto PP was determined to be 1 wt.%.

PU prepolymer was synthesized by the reaction of TDI with PPG. A typical procedure is described as follows. 2 mol of TDI was added to 1 mol of PPG under stirring and the mixture was heated at 80 °C for 6 h. By means of the amine equivalent method, the content of isocyanate groups of the PU prepolymer was determined to be 3.05 wt.%. The number average molecular weight of the PU prepolymer was 6.6×10^3, as checked by a Walter 208LC gel permeation chromatograph (GPC).

2.3. Preparation of PP masterbatches and composites

Firstly, PU prepolymer (11.3 g), MOCA (0.7 g), PP (30 g), and nano-SiO_2 (8 g) were dry-blended. Afterwards, the mixture was compounded in the mixer of a Haake Rheocord 300p (mixing temperature = 180 °C, rotor speed = 60 rpm, and mixing time = 10 min). Finally, the blends (namely SiO_2-g-PU/PU/PP masterbatches) were dried at 80 °C for 8 h. To evaluate the reaction between nano-SiO_2 and PU, a small amount of the masterbatches were extracted by refluxing xylene for one week. By using thermogravimetric analysis (TGA), the grafting percentage of the extracted residue (namely SiO_2-g-PU) was determined to be 37.14 wt.%. To reveal the effect of nano-SiO_2 in the composites, PU/PP masterbatches were also prepared in the absence of nano-SiO_2 according the above procedures.

To prepare PP based composites, SiO_2-g-PU/PU/PP and PU/PP masterbatches were compounded with PP and PP-g-NH_2 in the mixer of a Haake Rheocord 300p (mixing temperature = 180 °C, rotor speed = 60 rpm, and mixing time = 15 min), respectively. The resultant composites were named SiO_2-g-PU/PU/PP-g-NH_2/PP and PU/PP-g-NH_2/PP, respectively. For comparison, PP based composites without the reactive compatibilizer (PP-g-NH_2) were prepared using the same method yielding SiO_2/PP, SiO_2-g-PU/PU/PP, and PU/PP. Then, a Y-350 vertical injection molding machine was used to mold the compounds into standard bars for mechanical testing. The dimension of the deformable region of the tensile dumbbell specimens was $25.0 \times 3.2 \times 2.0$ mm^3. Rectangular bars with dimensions of $80 \times 10 \times 4$ mm^3 were used for impact tests. The bars were subsequently notched at the middle using a CSI cutter to produce "V" type notches with a depth of 2 mm.

It is worth noting that PU in SiO_2-g-PU/PU/PP-g-NH_2/PP and SiO_2-g-PU/PU/PP is individually highlighted because it was mixed with nano-SiO_2 at an excessive fraction. Besides the PU grafted onto the nanoparticles, the rest PU had to stay around the grafted nanoparticles as a rubber-like interphase.

2.4. Characterization

Fourier-transform infrared (FTIR) spectra of the samples were recorded on a Bruker EQUINOX 55 FTIR spectrometer. Blank scanning was performed prior to the measurements to eliminate the influence of water vapor and CO_2.

Thermogravimetric analysis (TGA) measurements were performed on a NETZSCH TG 209C thermogravimetric analyzer from 50 to 700 °C at a heating rate of 20 °C/min under a continuous flow of anhydrous nitrogen.

To assess dispersion of the nanoparticles in the matrix, ultrathin sections of the compounds were examined by a JEM-100CX II transmission electron microscope (TEM). In addition, fractured surfaces of the composites were observed by a JSM-6330F scanning electron microscope (SEM). Tensile properties of the composites were determined with a Hounsfield 10K-S universal tester at a crosshead speed of 50 mm/min according to ASTM D638-98. Notched Charpy impact strength was measured by an Atlas advanced pendulum impact device in accordance with ISO 179-2. All the specimens were stored at 30 °C and a relative humidity of 50% for 48 h prior to measurements at the same temperature and relative humidity.

3. Results and discussion

3.1. Evaluation of the in situ reactions

According to the route of composites manufacturing mentioned above, two-step in situ reaction was involved in the melt compounding. First, PU was grafted onto nano-SiO_2, and then the PU grafted nano-SiO_2 reacted with PP-g-NH_2 forming nano-SiO_2-PU-PP connections (Fig. 1). At the beginning of discussion, it should be confirmed whether the products of these reactions have been yielded as planned.

Fig. 2 collects FTIR spectra of the related substances. In the spectrum of PU prepolymer, the peaks at 3297 and 1731 cm^{-1} are the characteristic stretching peaks of N–H and C=O from urethane group, respectively. The strong peak at 2271 cm^{-1} is due to the adsorption of isocyanate group (—N=C=O). The multiple peaks at 2871–2972 cm^{-1} correspond to the stretching mode of C–H in –CH_2–, –CH–, and –CH_3, and the peaks at 1344–1453 cm^{-1} illustrate the bending modes of –CH_2– and –CH_3. The peak at 1107 cm^{-1} is assigned to the stretching mode of C–O–C. The peaks at 1539 and 1597 cm^{-1} represent phenyl groups. These results clearly confirm that isocyanate terminated PU prepolymer has been yielded.

By comparing the spectrum of SiO_2-g-PU with that of SiO_2, it is seen that the characteristic adsorptions of PU appear on the former (i.e. the multiple peaks at 2820–2975 cm^{-1} corresponding to the stretching modes of C–H in –CH_2–, –CH–, and –CH_3; the peaks at 1376–1457 cm^{-1} for the bending modes of –CH_2–, and –CH_3; the peaks at 1475 and 1646 cm^{-1} assigning to –NHCOO– groups; and the peak at 1532 cm^{-1} representing phenyl groups). Therefore, PU must have been successfully grafted onto silica nanoparticles.